

Photoionization mass spectrometric studies of the isomeric transient species CH_2SH and CH_3S

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(Received 16 March 1992; accepted 21 April 1992)

The products of the reaction of F atoms with CH_3SH are studied by photoionization mass spectrometry. Two thresholds, at 7.536 ± 0.003 eV and 9.262 ± 0.005 eV, are observed at mass 47, and identified with the adiabatic ionization potentials of CH_2SH and CH_3S , respectively. These conclusions are confirmed by additional experiments with CD_3SH , where an adiabatic ionization potential of 7.522 ± 0.003 eV is obtained at mass 49 (CD_2SH^+) and a value of 9.268 ± 0.005 eV is found at mass 50 (CD_3S^+). From an earlier appearance potential for CH_2SH^+ (CH_3SH) and the present ionization potential of CH_2SH , an upper limit for $D_0(\text{H}-\text{CH}_2\text{SH})$ of $\leq 93.97 \pm 0.13$ kcal/mol is deduced. By giving weight to the measured proton affinity of CH_2S , one obtains $D_0(\text{H}-\text{CH}_2\text{SH}) = 92.4 \pm 2.0$ kcal/mol. The corresponding S-H bond energy in CH_3SH derived from a recent kinetics-based value for $\Delta H_f^0(\text{CH}_3\text{S})$ is 86.1 ± 0.6 kcal/mol. A discrepancy in the difference of $\Delta H_f^0(\text{CH}_3\text{S}^+)$ and $\Delta H_f^0(\text{CH}_2\text{SH}^+)$ arising from recent theoretical and experimental determinations is resolved in favor of the *ab initio* values.

I. INTRODUCTION

Recently, there has been an upsurge of interest in the thermochemistry of organosulfur species, motivated at least in part by the emission of sulfur-containing pollutants from the combustion of sulfur-containing fuels. Ng and collaborators¹ have utilized two techniques: (1) laser photofragmentation of a supersonic neutral beam with time-of-flight detection of products and their kinetic energies, and (2) vacuum-ultraviolet photoionization mass spectrometry, to produce data on the heats of formation of neutral radical species and their cations. In some experiments,² they have combined the two techniques, producing radicals by laser photodissociation, and photoionizing the radicals. Thus, utilizing a pulsed beam of CH_3SCH_3 as the sample and 193 nm laser light, they generate CH_3S ($+\text{CH}_3$), and then determine the photoion yield curve of CH_3S^+ (CH_3S). In this way, they obtain a value for the adiabatic ionization potential of CH_3S (1344 ± 2 Å $\equiv 9.225 \pm 0.014$ eV).² In previous photofragmentation experiments utilizing CH_3SH , CH_3SCH_3 , and CH_3SSCH_3 , they deduced $\Delta H_f^0(\text{CH}_3\text{S}) = 35.0 \pm 1.0$ kcal/mol. Combining these values, they arrive at $\Delta H_f^0(\text{CH}_3\text{S}^+) = 247.7 \pm 1.1$ kcal/mol.

One might imagine that this quantity could be directly obtained from appearance potential measurements such as



However, it has been shown by collisional activation experiments,³ charge transfer,⁴ and by *ab initio* calculations⁵ that the isomeric form CH_2SH^+ is significantly more stable, and is the species observed at threshold. This parallels the behavior of the corresponding oxyhydrocarbons— CH_2OH^+ is significantly more stable than CH_3O^+ .⁶

Nicovich *et al.*⁷ studied the kinetics of bromination of CH_3SH , CH_3SCH_3 , and CH_3SSCH_3 . One of their findings is that CH_3S , rather than CH_2SH , is formed upon reacting

bromine with CH_3SH , and hence CH_3S is more stable than CH_2SH . This behavior is opposite to that of the corresponding oxygen species— CH_2OH is more stable than CH_3O . Furthermore, Nicovich *et al.*⁷ obtain $\Delta H_f^0(\text{CH}_3\text{S}) = 29.9 \pm 0.3/29.4 \pm 0.6$ kcal/mol (second- and third-law values) or $\Delta H_f^0(\text{CH}_3\text{S}) = 31.44 \pm 0.54$ kcal/mol, significantly lower than the value (35.0 ± 1.0 kcal/mol) reported by Nourbakhsh *et al.*²

The magnitude of $\Delta H_f^0(\text{CH}_2\text{SH})$ is still in doubt. However, $\Delta H_f^0(\text{CH}_2\text{SH}^+)$ has been determined by several groups. Nourbakhsh *et al.*² state that the literature value for $\Delta H_f^0(\text{CH}_2\text{SH}^+)$ is in the range 206–209 kcal/mol. Their own values, included in this literature, are at the lower end of this range. In fact, they give $\Delta H_f^0(\text{CH}_2\text{SH}^+) = 204.5 \pm 1.2$ kcal/mol from appearance energy measurements on CH_3SH ,¹ and $\Delta H_f^0(\text{CH}_2\text{SH}^+) = 206.2 \pm 1$ kcal/mol from appearance energy measurements on CH_3SCH_3 .¹ If we restrict ourselves for the moment to the recent values of Nourbakhsh *et al.*^{1,2} for $\Delta H_f^0(\text{CH}_3\text{S}^+)$ and $\Delta H_f^0(\text{CH}_2\text{SH}^+)$, we arrive at a difference of (41.5–43.2) ± 1.6 kcal/mol.

Nobes and Radom,⁸ allowing for the 206–209 kcal/mol flexibility in $\Delta H_f^0(\text{CH}_2\text{SH}^+)$, choose an experimental difference in the heats of formation of the isomeric cations from Nourbakhsh *et al.* to be somewhat lower, 39.0–41.1 kcal/mol. Nevertheless, their *ab initio* calculated difference at the Gaussian 2 (G2) level of theory, ≤ 33.0 kcal/mol, is significantly lower than that of Nourbakhsh *et al.* Upon more detailed analysis, they find that their calculated value of $\Delta H_f^0(\text{CH}_3\text{S}^+)$ is lower by about 5 kcal/mol, while their calculated value of $\Delta H_f^0(\text{CH}_2\text{SH}^+)$ is higher by about 5 kcal/mol, than the values obtained by Nourbakhsh *et al.*² Hence, they question not only the difference in heats of formation, but each value separately.

We⁶ recently prepared CH_3O and CH_2OH by the reac-

tion of F atoms with CH₃OH, and studied these isomeric species by photoionization mass spectrometry. Several prior studies⁹⁻¹¹ indicated that the reaction of F atoms with CH₃SH should proceed analogously, generating both CH₂SH and CH₃S. Using selectively deuterated species, we hoped to measure the previously undetermined ionization energy of CH₂SH, and to check the ionization potential of CH₃S. With these measurements, and a critical examination of existing literature values, we hoped to resolve the discrepancy between *ab initio* theory and experiment for $\Delta H_f^0(\text{CH}_3\text{S}^+)$ and $\Delta H_f^0(\text{CH}_2\text{SH}^+)$. From the measured ionization energy of CH₂SH, the heat of formation of the neutral species would also be established.

II. EXPERIMENTAL ARRANGEMENT

Experiments were performed with both CH₃SH and CD₃SH. The transient species CH₃S (CD₃S) and CH₂SH (CD₂SH) were prepared *in situ* by reactions of F atoms with CH₃SH (CD₃SH). The fluorine atoms were generated in a microwave discharge through pure F₂. The description of the flow tube and reaction cup has been given previously, as has the photoionization mass spectrometric method.¹² The measurements were performed utilizing the peak light intensities in the many-line emission spectrum of a discharge in molecular hydrogen. The nominal wavelength resolution was kept at 0.84 Å (full width at half maximum). The sample of CH₃SH was from Aldrich (99.5 + % purity), while CD₃SH was obtained from MSD Isotopes, and had a stated D atom purity of 99%.

III. EXPERIMENTAL RESULTS

A. Experiments with CH₃SH

The anticipated products from reaction with F atoms, CH₂SH and CH₃S, would both appear at mass 47 upon photoionization. In the analogous study of CH₂OH and CH₃O, it was found that CH₃O⁺ could not be observed, although CD₃O⁺ was detected.⁶ The CH₃O⁺ was inferred to decompose on a time scale of several μs. Hence, it was not clear *a priori* if CH₃S⁺ could be observed.

Figure 1 is a display of the photoion yield curve at mass

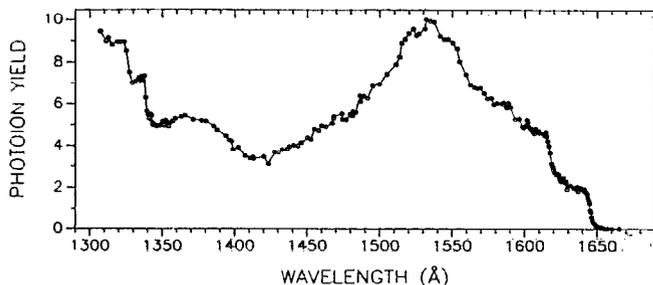
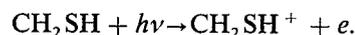
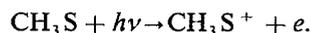


FIG. 1. The photoion yield curve of mass 47 monitored during the reaction of F atoms with CH₃SH. It is shown (see text) that the wavelength region between ~1340 and 1660 Å is attributable to the process CH₂SH + *hν* → CH₂SH⁺ + *e*, while the growth in the region below ~1340 Å is primarily attributable to the process CH₃S + *hν* → CH₃S⁺ + *e*.

47, subsequent to the F + CH₃SH reaction. The wavelength range shown (1300–1600 Å) corresponds to a photon energy (9.5–7.5 eV) much less than is required (~11.5 eV) for dissociative ionization of CH₃SH to produce mass-47 ions. At the long-wavelength end of the spectrum, at least two broad, steplike features appear, which may be attributable to a Franck–Condon vibrational progression in the cation. Their separation corresponds to a vibrational frequency of $\sim 1020 \pm 40 \text{ cm}^{-1}$. There is a bulge above experimental scatter at $\sim 1629 \text{ Å}$, and perhaps another at $\sim 1603 \text{ Å}$, giving a hint of another progression of $\sim 600 \pm_{40}^{80} \text{ cm}^{-1}$. The steps display curvature, which we attribute to rotational broadening. The half-rise in the first step, which would approximate the top of the peak in a photoelectron spectrum, occurs at $1645.3 \pm 0.7 \text{ Å} \equiv 7.536 \pm 0.003 \text{ eV}$. We attribute this onset, and the ensuing photoion yield curve down to $\sim 1340 \text{ Å}$, to the process



This conclusion is based partly on the analogous behavior of the oxygenated species (CH₂OH has a much lower ionization potential than CH₃O), and to the fact that Nourbakhsh *et al.*² obtained a much higher value (9.225 eV) for the ionization of the isomeric CH₃S. In fact, there is an increase in the photoion yield at about the energy observed by Nourbakhsh *et al.*, which we tentatively attribute to the process



Hence, unlike the CH₃O⁺ case, the CH₃S⁺ ion appears to be (meta)stable.

At shorter wavelength, there is a broad maximum centered at $\sim 1535 \text{ Å}$, and perhaps a second broad band at $\sim 1365 \text{ Å}$. These could be vibrationally broadened members of a Rydberg series converging to the first excited state of CH₂SH⁺.

At about 1340 Å, a new series of steps appears, which we have tentatively assigned to the onset of ionization from the isomeric CH₃S, pending a confirmatory study of CD₃SH. The spacing of the steps, attributed to a vibrational progression in CH₃S⁺, is about $700 \pm 60 \text{ cm}^{-1}$. The first step displays a weak bump at the threshold and a rather sharp (rather than rounded) character at the top of the step, which may result from weak autoionization. We choose the half-rise point, as before, which occurs at $1338.6 \pm 0.7 \text{ Å} \equiv 9.262 \pm 0.005 \text{ eV}$, as the adiabatic ionization potential of CH₃S.

B. Experiments with CD₃SH

1. Mass 50, CD₃S⁺

If both isomeric species are formed by the F + CD₃SH reaction, then CD₃S⁺ would appear at mass 50, CD₂SH⁺ at mass 49. The photoion yield curve at mass 50 during these experiments appears in Fig. 2(a). It is immediately apparent that the structure in the photoion yield curve of Fig. 1 above $\sim 1345 \text{ Å}$ [repeated as Fig. 2(b)] is much weaker in Fig. 2(a). In fact, the residual “tail” above $\sim 1345 \text{ Å}$ in Fig. 2(a) can be followed all the way to $\sim 1650 \text{ Å}$ and closely resem-

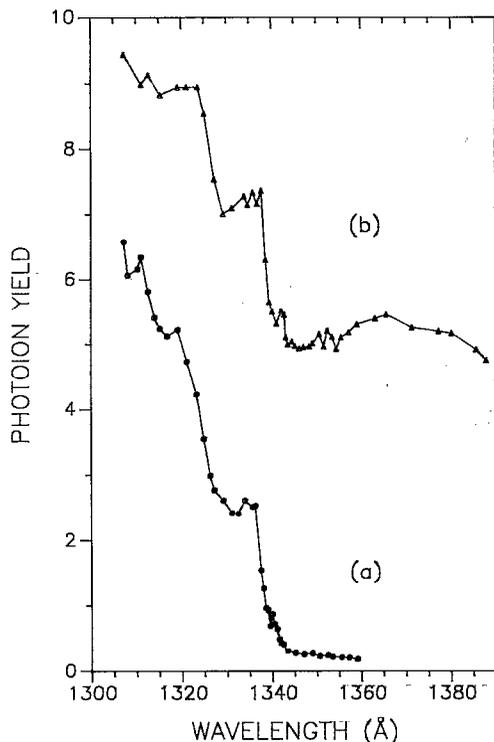


FIG. 2. (a) The photoion yield curve at mass 50, monitored during the reaction of F atoms with CD_3SH . This photoion yield curve is attributed to the process $\text{CD}_3\text{S} + h\nu \rightarrow \text{CD}_3\text{S}^+ + e$. (b) An expanded portion of the photoion yield curve from Fig. 1, attributed to $\text{CH}_3\text{S} + h\nu \rightarrow \text{CH}_3\text{S}^+ + e$. Note the similarity in structure between curves (a) and (b), and the much lower "background" above 1340 Å in curve (a).

bles the curves of CH_2SH^+ (CH_2SH) in Fig. 1 and CD_2SH^+ (CD_2SH) in Fig. 3 (see below), but is about 35 times weaker. The structure below ~ 1345 Å in Fig. 1 [or Fig. 2(b)] closely matches that in Fig. 2(a). This circumstance provides definite proof for the assignments given earlier, namely that the photoion yield curve between ~ 1345 and 1665 Å refers to CH_2SH^+ , and that below ~ 1345 Å refers primarily to CH_3S^+ (CH_3S) superimposed on a relatively featureless "background" of CH_2SH . The threshold region of the photoion yield curve of Fig. 2(a) displays a bump similar to that discussed for Figs. 1 and 2(b). The first step appears more rectilinear than the corresponding feature in Fig. 2(b). The half-rise is chosen as 1337.8 ± 0.7 Å $\equiv 9.268 \pm 0.005$ eV. The interval between steps is roughly 730 ± 60 cm^{-1} , perhaps somewhat higher than that obtained from the CH_3S^+ spectrum.

2. Mass 49, CD_2SH^+

This photoion yield curve, attributed to CD_2SH^+ (CD_2SH), is shown in Fig. 3. A series of steplike features appears in the threshold region, characteristic of direct photoionization. At least two types of spacings, with energy separations of 900 ± 40 cm^{-1} and 490 ± 40 cm^{-1} , can be distinguished. The half-rise in the first step, which we take to be the adiabatic ionization potential, occurs at 1648.3 ± 0.7 Å $\equiv 7.522 \pm 0.003$ eV. Thus, the ionization potential of

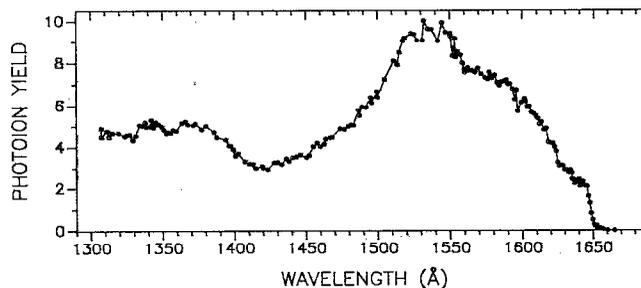


FIG. 3. The photoion yield curve at mass 49, monitored during the reaction of F atoms with CD_3SH . This photoion yield curve is attributed to the process $\text{CD}_2\text{SH} + h\nu \rightarrow \text{CD}_2\text{SH}^+ + e$.

CD_2SH is redshifted from that of CH_2SH by about 0.014 eV.

At shorter wavelengths, a broad band is evident, with a maximum at ~ 1535 Å, and then two weaker broad bands with maxima at ~ 1365 and ~ 1340 Å. The first two broad bands match those observed in CH_2SH^+ (CH_2SH). Very roughly, these bands could be identified with Rydberg members forming a series converging to a second ionization potential (I.P.), with a vertical I.P. of ~ 10.2 eV.

The adiabatic ionization potentials of CH_2SH , CH_3S , and their deuterated variants are summarized in Table I.

IV. INTERPRETATION OF RESULTS

A. CH_2SH (CD_2SH)

The adiabatic ionization potential of CH_2SH obtained in this work is 7.536 ± 0.003 eV. We are unaware of any prior measurement of this quantity. This value for CH_2SH is very close to that obtained previously for CH_2OH ,⁶ 7.549 ± 0.006 eV. The implication is that ionization occurs from an unpaired electron localized near the carbon atom. The adiabatic ionization potential of CD_2SH determined here is 7.522 ± 0.003 eV, lower than that of the protonated form by ~ 0.014 eV. Curtiss and co-workers¹³ calculated vibrational frequencies for CH_2SH , CD_2SH , and the respective cations. From the differences in zero-point energies, one obtains $\text{I.P.}(\text{CH}_2\text{SH}) - \text{I.P.}(\text{CD}_2\text{SH}) = 0.014$ eV, in excellent agreement with the experimental observation.

A primary vibrational progression of about 1020 ± 40 cm^{-1} is inferred for CH_2SH^+ . In the photoelectron spectrum of CH_2OH , Dyke and co-workers¹⁴ observed a pri-

TABLE I. Adiabatic ionization potentials of CH_2SH (CD_2SH) and CH_3S (CD_3S).

Species	I.P. (eV)
CH_2SH	7.536 ± 0.003^a
CD_2SH	7.522 ± 0.003^a
CH_3S	$9.262 \pm 0.005^a, 9.225 \pm 0.014^b$
CD_3S	9.268 ± 0.005^a

^a Present results.

^b Reference 2.

mary vibrational progression of $1650 \pm 30 \text{ cm}^{-1}$, which they attributed to the C–O stretch, increased from the value (1183 cm^{-1}) in the neutral species. A similar behavior is inferred here, i.e., the C–S stretch in CH₂SH⁺ is taken to be $\sim 1020 \text{ cm}^{-1}$, increased from its value in the neutral species.¹⁵ The primary vibrational progression in CD₂SH⁺ ($900 \pm 40 \text{ cm}^{-1}$) is slightly smaller than that in CH₂SH⁺, implying the involvement of some hydrogen motion in the normal coordinate associated with this frequency. Recent *ab initio* calculations¹³ indicate that the major change upon ionization is the reduction of the C–S bond length by $\sim 0.1 \text{ \AA}$. This is expected to result in an increase in the C–S stretching frequency, as observed.

B. CH₃S (CD₃S)

The adiabatic ionization potential of CH₃S (CD₃S) obtained in this work is $9.262 \pm 0.005 \text{ eV}$ ($9.268 \pm 0.005 \text{ eV}$), i.e., there is a small blueshift in the deuterated species. As in the analogous case of CH₃O, there is believed to be very little change in geometrical structure upon ionization, according to *ab initio* calculations.¹³ Therefore, the 0–0 Franck–Condon band should be strong. The value of the adiabatic I.P. given by Nourbakhsh *et al.* ($1344 \pm 2 \text{ \AA} \equiv 9.225 \pm 0.014 \text{ eV}$) lies at the very bottom of the tail in our spectrum, even below the bump. The vibrational interval of $\sim 700\text{--}730 \text{ cm}^{-1}$ could be a C–S stretch, not greatly different from that (707 cm^{-1})¹⁵ in the neutral species. The apparent increase in this frequency upon deuteration, though surprising, is consistent with the observed blueshift in the ionization potential. From photodetachment studies of CH₃S[−] and CD₃S[−], Janousek and Brauman¹⁶ assign vibrational frequencies of $770 \pm 50 \text{ cm}^{-1}$ and $660 \pm 60 \text{ cm}^{-1}$ to the C–S stretch in the protonated and deuterated samples, respectively. Engelking, Ellison, and Lineberger,¹⁷ from similar experiments on CH₃S[−], assign $680 \pm 40 \text{ cm}^{-1}$ to the C–S stretch.

The bump, which appears in both the CH₃S and CD₃S experiments, appears lower than the chosen I.P.'s by $240 \pm 50 \text{ cm}^{-1}$ and $210 \pm 50 \text{ cm}^{-1}$, respectively, and the intensity is $\sim 1/3$ as large as the first major step. Hsu, Liu, and Miller¹⁸ have extracted -255.5 cm^{-1} as the effective spin–orbit splitting in CH₃S from their spectrum, somewhat higher than the microwave value,¹⁹ $-221.0 \pm 2.0 \text{ cm}^{-1}$. In previous abstraction reactions in our apparatus, the temperature of the transient species was found to be near 298 K. The spin–orbit splitting of Hsu, Liu, and Miller corresponds to $\sim 29\%$ abundance of the excited spin–orbit component, assuming Boltzmann conditions at 298 K. Hence, it is quite likely that the bump corresponds to photoionization of this excited spin–orbit component. This observation provides additional support for our choice of the adiabatic I.P.

It is conceivable that the photoionization experiment of Nourbakhsh *et al.*,² which involved laser photodissociation of CH₃SCH₃, produced primarily the excited spin–orbit component, thereby accounting for their lower value. However, their sample of CH₃S was cooled by supersonic expansion, which should have depopulated the excited state. A more likely explanation is that their lower resolution (1.5

\AA), larger spacing between points, and their actual choice of threshold at the very onset of ionization accounts for their lower value.

V. DISCUSSION OF RESULTS

A. $\Delta H_f^0(\text{CH}_2\text{SH}^+)$ and $\Delta H_f^0(\text{CH}_2\text{SH})$

In Table II, we list some recent literature values for $\Delta H_f^0(\text{CH}_2\text{SH}^+)$. The values of Nourbakhsh *et al.*² are distinctly lower than the other values. Their experimental value of 204.5 kcal/mol is based on the appearance potential of CH₂SH⁺ from CH₃SH, essentially the same experiment as performed previously by Kutina *et al.*²⁰ The latter authors select the intersection of a rapidly rising linear portion of the photoion yield curve to the background level, and arrive at $1073.5 \pm 0.5 \text{ \AA} \equiv 11.550 \pm 0.005 \text{ eV}$, modified to $11.611 \pm 0.005 \text{ eV}$ at 0 K. Furthermore, Kutina *et al.*²⁰ explicitly mention that they investigated the pressure dependence of the very weak tail extending below the threshold and concluded that it originates in higher-order collisional processes. Nourbakhsh *et al.*¹ select $1104 \pm 5 \text{ \AA} \equiv 11.23 \pm 0.05 \text{ eV}$ as their threshold. In their Fig. 8(b), this choice is well below the intersection of the linearly rising portion and the background level. Nourbakhsh *et al.*¹ attribute the rapid linear increase in CH₂SH⁺ (CH₃SH) to the onset of the second photoelectron band of CH₃SH, at $\sim 11.5 \text{ eV}$. Perhaps the clearest He I photoelectron spectrum of CH₃SH is that of Cradock and Whiteford.²¹ The second photoelectron band does indeed have an adiabatic threshold near $\sim 11.5 \text{ eV}$. However, a careful reading shows that it extends significantly below 11.5 eV , and at 11.611 eV (the value chosen by Kutina *et al.*²⁰) one is well inside the band. Furthermore, photoionization is (in first approximation) an integral over a photoelectron spectrum, and hence the tailing region of the photoelectron band will be steeper in photoionization. If the rapid linear increase in CH₂SH⁺ is due entirely to this band, its onset should occur at a lower value than observed.

Nourbakhsh *et al.*¹ choose to disregard their own coincidence experiments, which display an onset for CH₂SH⁺

TABLE II. Alternative literature values for $\Delta H_f^0(\text{CH}_2\text{SH}^+)$, in kcal/mol.

$\Delta H_{f_{\text{vib}}}^0$ (CH ₂ SH ⁺)	ΔH_f^0 (CH ₂ SH ⁺)	Method and citation
206 ± 2	208 ± 2	Photoionization (Ref. 22)
208 ± 1	$(210 \pm 1)^a$	Electron impact (Ref. 23)
	< 213.1	Photoionization (Ref. 20)
208 ± 1	$(210 \pm 1)^{a,b}$	Charge-transfer ladder (Refs. 4 and 8)
	204.5 ± 1.2	Photoionization, CH ₃ SH (Ref. 1)
	206.2 ± 1	Photoionization, CH ₃ SCH ₃ (Ref. 1)

^aWe have applied a correction of 2 kcal/mol to the $\Delta H_{f_{\text{vib}}}^0$ values given in this citation, in order to convert to ΔH_f^0 , and thereby have a uniform basis of comparison. Our calculated correction is 1.82 kcal/mol .

^bThe relative proton affinity of CH₂S (Ref. 4) was combined with the calculated $\Delta H_f^0(\text{CH}_2\text{S})$ from Ref. 8 to arrive at $\Delta H_f^0(\text{CH}_2\text{SH}^+)$.

(CH₃SH) at $\sim 1077 \text{ \AA} \equiv 11.51 \text{ eV}$. They presumably believe that the true onset is too weak to be observed, due to the Franck–Condon gap. However, there is evidence in their coincidence spectrum that parent ion is still being observed until $\sim 1077 \text{ \AA}$, below which it declines and CH₂SH⁺ increases, as expected for the onset of fragmentation.

There is still a more convincing argument against the choice of Nourbakhsh *et al.* The CH₂S⁺ (CH₃SH) fragment appears at a lower energy than CH₂SH⁺ (CH₃SH). Therefore, its intensity suffers more from the Franck–Condon gap, yet it is clearly seen in the experiments of Kutina *et al.*²⁰ and Nourbakhsh *et al.*¹ In both experiments, the photoion yield curve of CH₂S⁺ manifests a rapid linear increase at the onset of the second photoelectron band of CH₃SH, and then a cusp at $\sim 11.6 \text{ eV}$. There is nothing in the photoelectron spectrum that suggests such a cusp. However, the cusp matches the observed onset of CH₂SH⁺. The obvious interpretation is that the CH₂S⁺ channel begins to suffer competition from the new channel (CH₂SH⁺) at just the energy corresponding to the cusp. This is the expected behavior when a simple bond rupturing process competes with a more constrained fragmentation having a lower threshold, and was already mentioned by Kutina *et al.*²⁰

Butler, Baer, and Evans²² and Holmes *et al.*²³ also base their values on appearance potentials, the first by photoionization and the latter by electron impact. The value inferred from Roy and McMahon⁴ ($210 \pm 1 \text{ kcal/mol}$ at 0 K) is based on the proton affinity ladder and a calculated $\Delta H_{f_0}^0(\text{CH}_2\text{S})$ from Nobes and Radom⁸ and consequently is independent of the problems associated with the interpretation of thresholds. The *ab initio* calculated value¹³ (211.7 kcal/mol) is between that of Roy and McMahon⁴ (and also that of Holmes *et al.*²³) and the upper limit of $213.1 \pm 0.2 \text{ kcal/mol}$ obtained from the Kutina *et al.*²⁰ threshold. Although the upper limit remains rigorous, we choose here an average value for $\Delta H_{f_0}^0(\text{CH}_2\text{SH}^+)$ of $211.5 \pm 2.0 \text{ kcal/mol}$. With this value, and our adiabatic ionization potential for CH₂SH, we deduce $\Delta H_{f_0}^0(\text{CH}_2\text{SH}) = 37.7 \pm 2.0 \text{ kcal/mol}$.

B. $\Delta H_{f_0}^0(\text{CH}_3\text{S})$ and $\Delta H_{f_0}^0(\text{CH}_3\text{S}^+)$

As discussed in the Introduction, Nourbakhsh *et al.*² give $35.0 \pm 1.0 \text{ kcal/mol}$ for $\Delta H_{f_0}^0(\text{CH}_3\text{S})$, while the second- and third-law kinetics-based value of Nicovich *et al.*⁷ is $31.44 \pm 0.54 \text{ kcal/mol}$. From the highest vibrational and rotational levels of HF observed in the F + CH₃SH reaction, Dill and Heydtmann⁹ conclude that $\Delta H_{f_0}^0(\text{CH}_3\text{S}) \leq 30.6 \text{ kcal/mol}$. Another less-precise value can be extracted from the gas-phase acidity of CH₃SH ($359.0 \pm 2 \text{ kcal/mol}$) given by Bartmess, Scott, and McIver,²⁴ the electron affinity of CH₃S ($1.861 \pm 0.004 \text{ eV}$) obtained by Janousek and Brauman,¹⁶ and auxiliary data. Thus, $\Delta H_{f_0}^0(\text{CH}_3\text{S}^-) = -10.5 \pm 2 \text{ kcal/mol}$ and $\Delta H_f^0(\text{CH}_3\text{S}) = 32.5 \pm 2 \text{ kcal/mol}$. If we combine the value of Nicovich *et al.*⁷ with the adiabatic ionization potential of CH₃S obtained in the present work, we deduce $\Delta H_{f_0}^0(\text{CH}_3\text{S}^+) = 245.0 \pm 0.5 \text{ kcal/mol}$. Using various cycles, Nobes and Radom⁸ calcu-

late 243.1, 242.3, and 241.4 kcal/mol for this quantity, settling upon $242.4 \pm 2.5 \text{ kcal/mol}$. Subsequently, Curtiss and co-workers¹³ modified this calculated value to 243.8 kcal/mol. Since these calculations on similar molecules have achieved accuracies of $\pm 2 \text{ kcal/mol}$, the agreement between experiment and theory in the present case is quite satisfactory. If the value of $\Delta H_{f_0}^0(\text{CH}_3\text{S})$ given by Nourbakhsh *et al.*² were used, there would be a discrepancy of 4–5 kcal/mol between theory and experiment.

C. Difference in stabilities of CH₂SH, CH₃S, and their cations

From the experimentally based values of $\Delta H_{f_0}^0(\text{CH}_3\text{S}^+) = 245.0 \pm 0.5 \text{ kcal/mol}$ and $\Delta H_{f_0}^0(\text{CH}_2\text{SH}^+) = 211.5 \pm 2.0$ and $\leq 213.2 \text{ kcal/mol}$, we obtain a difference of $33.5 \pm 2.0 \text{ kcal/mol}$. Nobes and Radom⁸ obtain $\leq 33.0 \text{ kcal/mol}$ for this difference, while the value of Nourbakhsh *et al.*² is about $40 \pm 2 \text{ kcal/mol}$. Hence, based on the data and arguments given above, the discrepancy between experiment and *ab initio* calculation would appear to be resolved in favor of the *ab initio* value.

Taking $\Delta H_{f_0}^0(\text{CH}_3\text{S}) = 31.44 \pm 0.5 \text{ kcal/mol}$ from Nicovich *et al.*⁷ and $37.7 \pm 2.0 \text{ kcal/mol}$ for $\Delta H_{f_0}^0(\text{CH}_2\text{SH})$, we find that CH₃S is more stable by $6.3 \pm 2.0 \text{ kcal/mol}$.

Shum and Benson²⁵ noted that the C–H bond strength in organic sulfur compounds had never been measured. From kinetic studies of the I₂ + CH₃SCH₃ reaction, they cited a preliminary value of $96 \pm 1 \text{ kcal/mol}$ for the C–H bond strength. Applying this value to the C–H bond strength in CH₃SH, one obtains $\Delta H_{f_{298}}^0(\text{CH}_2\text{SH}) = 38.4 \pm 1 \text{ kcal/mol}$, 7.4 kcal/mol higher than their adopted value for $\Delta H_{f_{298}}^0(\text{CH}_3\text{S})$, $31.0 \pm 1 \text{ kcal/mol}$. Nicovich *et al.*,⁷ citing Dill and Heydtmann⁹ and Shum and Benson,²⁵ state that “the C–H bond in CH₃SH is thought to be about 6 kcal/mol stronger than the S–H bond.” The difference in stabilities of CH₃S and CH₂SH implied by these measurements is consistent with our deduced value, $6.3 \pm 2.0 \text{ kcal/mol}$.

From measurements of the appearance potential A.P.(CH₂SH⁺)/CH₃SH $\leq 11.611 \pm 0.005 \text{ eV}$ and I.P.(CH₂SH) = $7.536 \pm 0.003 \text{ eV}$ made in our laboratory, we can arrive by simple subtraction at an upper limit to the C–H bond strength in CH₃SH, $D_0(\text{H–CH}_2\text{SH}) \leq 4.075 \pm 0.006 \text{ eV} \equiv 93.97 \pm 0.13 \text{ kcal/mol}$. If we use the probable value for $\Delta H_{f_0}^0(\text{CH}_2\text{SH}) = 37.7 \pm 2.0 \text{ kcal/mol}$ deduced in Sec. V B, the C–H bond energy becomes $92.4 \pm 2.0 \text{ kcal/mol}$. The S–H bond energy recently obtained by Nicovich *et al.*⁷ is $D_0(\text{CH}_3\text{S–H}) = 86.0 \pm 0.7 \text{ kcal/mol}$ [or, with our value for $\Delta H_{f_0}^0(\text{CH}_3\text{SH}) = -3.0 \pm 0.1 \text{ kcal/mol}$, $D_0(\text{CH}_3\text{S–H}) = 86.1 \pm 0.6 \text{ kcal/mol}$]. However, if one were to take A.P.(CH₂SH⁺/CH₃SH) = $11.23 \pm 0.05 \text{ eV}$ from Nourbakhsh *et al.*¹ and combine it with the present I.P. of CH₂SH, one would infer $D_0(\text{H–CH}_2\text{SH}) = 85 \pm 1 \text{ kcal/mol}$, i.e., a C–H bond energy which is less than, or at best equal to the S–H bond energy in CH₃SH. This is unlikely, in view of other known S–H and C–H bond energies.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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